Polymer transistors and TFT backplanes

R. A. Street

Palo Alto Research Center (PARC)

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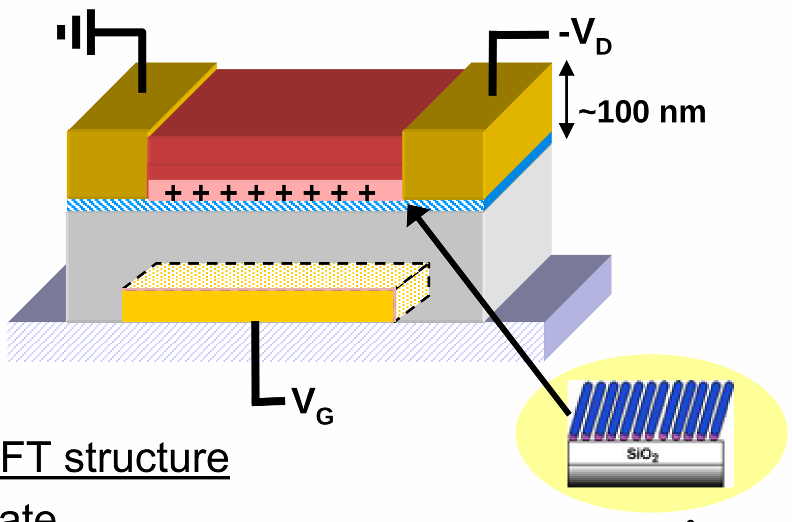
Outline

- Polymer TFTs on glass and flex
  - Materials
  - TFTs and backplanes
  - Plastic substrates and mechanical stress
- TFT mobility
  - Physical structure of films
  - Interfaces
  - Electronic structure
  - Transport models
- Transistor Lifetime
  - Bias stress effects
  - Chemical effects and encapsulation



<u>Typical TFT structure</u>

Bottom gate

Coplanar source/drain

Polymer deposited on SAM

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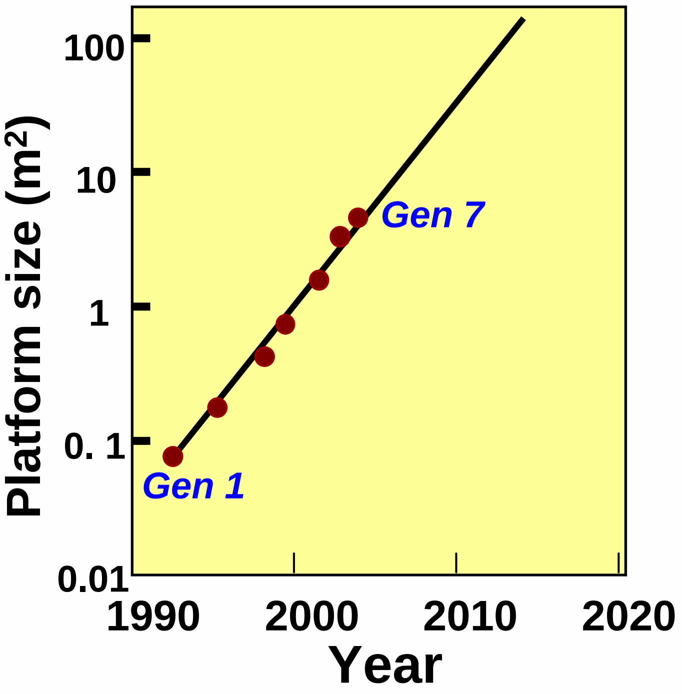
Motivation

- How many more generations before the cost outweighs the benefits?



Alternative technology

- Lower cost equipment → printing
- Less material use → additive processes
- R2R processing → flexible substrates
- New functionality → conformable, rollable, lightweight…..

→ Jet-printing
→ Printable materials
→ Flexible substrates

Applications, LCD, OLED, e-paper, signage etc

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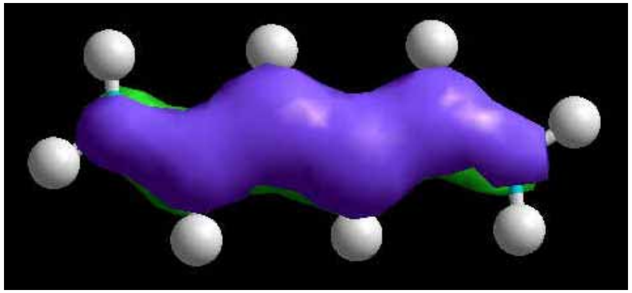
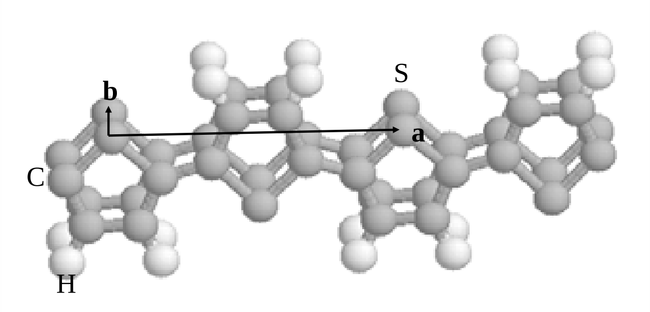
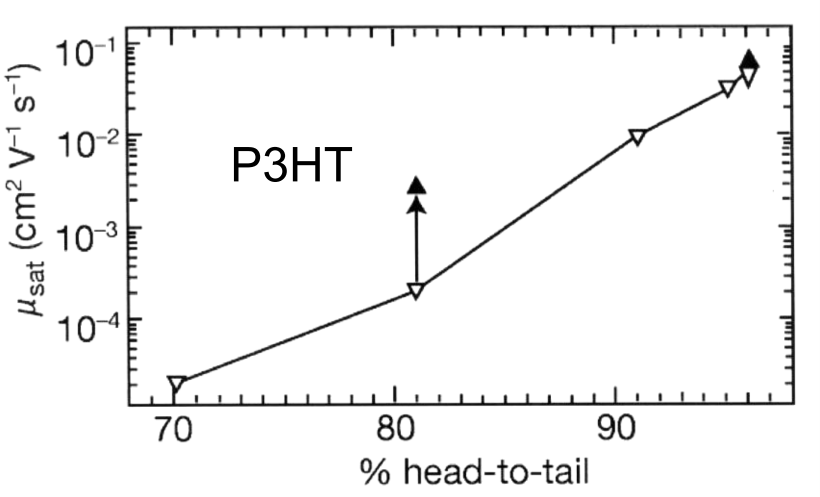
Soluble polymer semiconductors

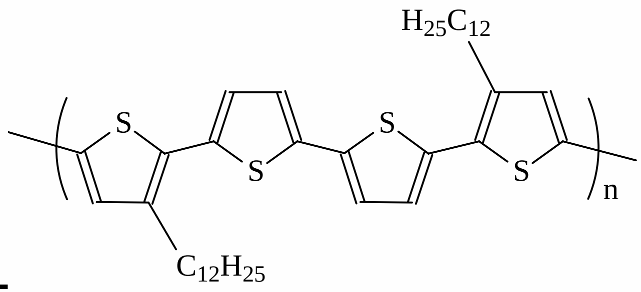
- Conjugated
  - Mostly p-type conduction, 1.5-2 eV band gap
- Alkyl side groups added for solubility
  - Regioregular
  - Polythiophene, PQT-12
- Structural order required for high mobility
  - π stacked lamella structure







H. Sirringhaus et al., Nature 401, 685 (1999)



PQT;

Ong et al. JACS, 126, 3378 (2004)

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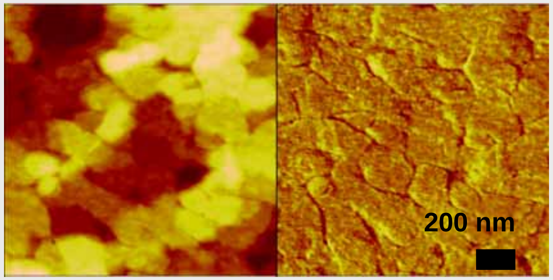
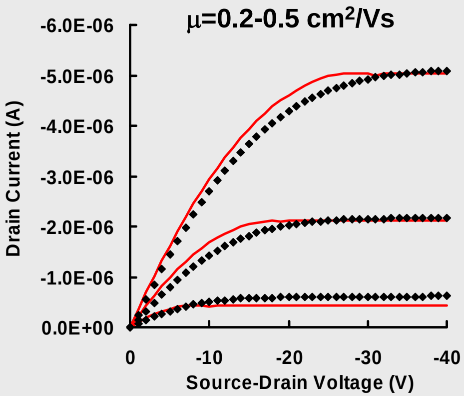
Polythiophene TFTs

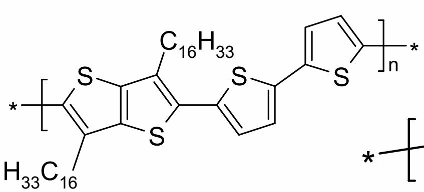
Merck material 180C anneal

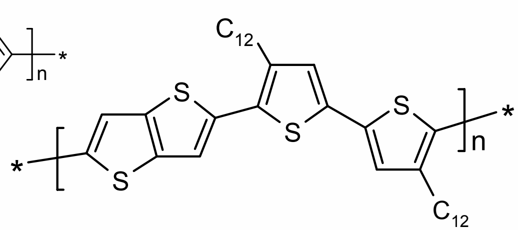


topography **phase**



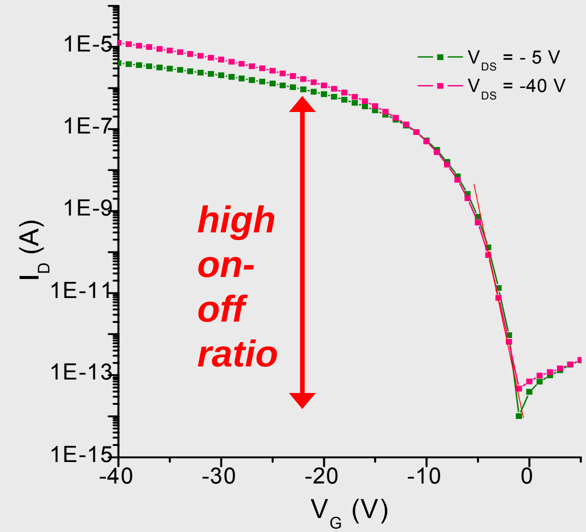
I. McCulloch, et. al. *Nat Mat.* 2006

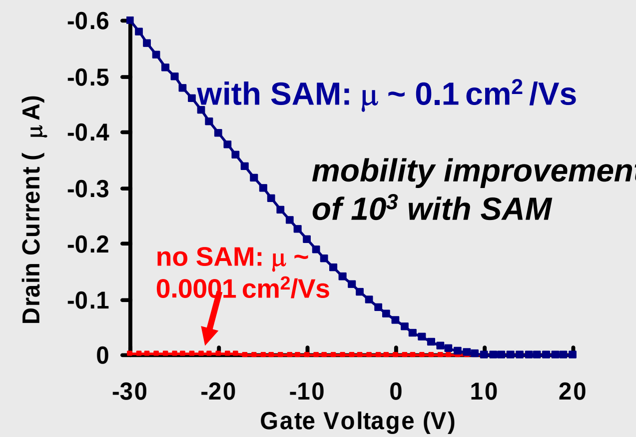




PQT

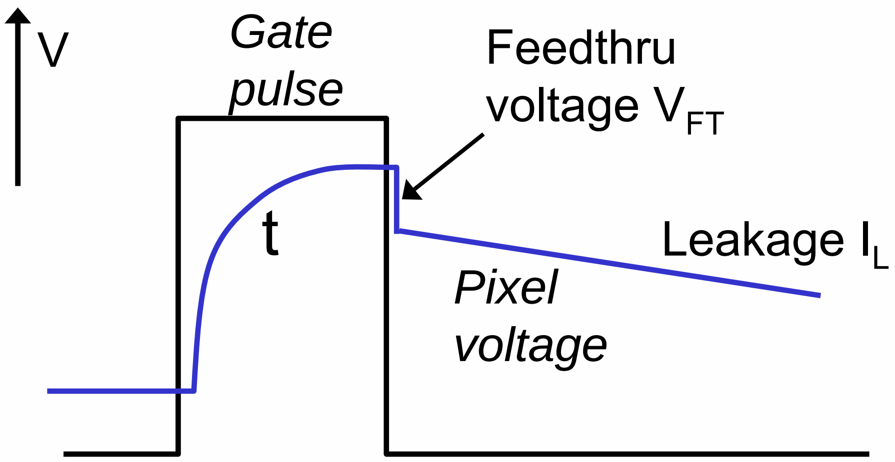
- Mobility 0.03-0.15 cm^2/Vs
  - Best on thermal oxide
  - Lower on large area dielectric





TFT Backplanes

- Capacitative displays; LCD, reflective
- Current drive; OLED



$V_{FT} = V_G \, C_{parasit}/C_{pix}$

$t = R_{TFT} \, . \, C_{pixel}$

$dV/dt = I_L/C_{pixel}$

Printing → large $C_{parasit}$ → Large C_{pixel} → high mobility

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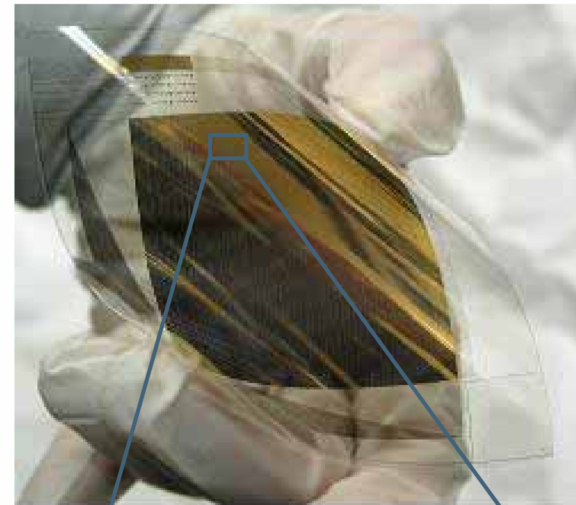
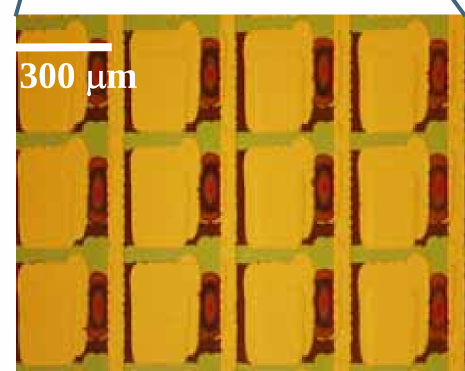
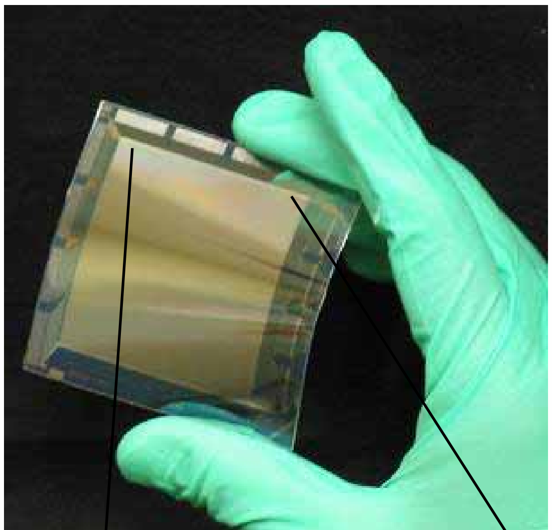
A-Si arrays on flex

Printed polymer array on flex

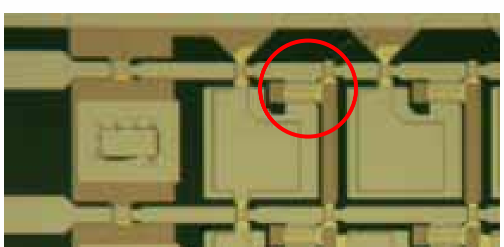




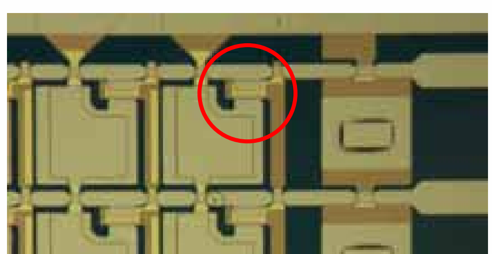
512x512 a-Si array on PEN



Upper left corner



Upper right corner

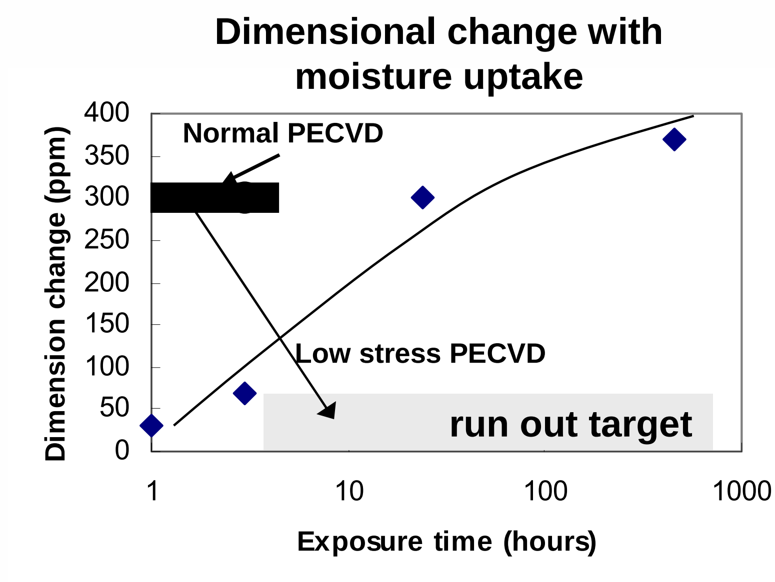


100 μm

Plastic substrates: Control of run-out

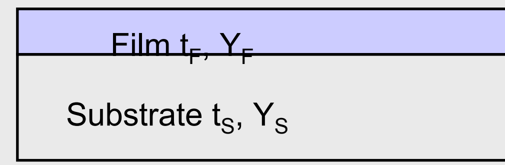
Dimensional stability of plastics is much poorer than glass or steel

- Run-out is induced by
  - mechanical stress in deposited film
    - » Thin film deposition
    - » Thermal expansion mismatch
  - Moisture uptake



Elastic modulus Y;

Glass	~100 GPa
Steel	~200 GPa
Plastic	~1-5 GPa



Run-out:

$$\varepsilon_S = \varepsilon_F \frac{Y_F t_F}{Y_S t_S + Y_F t_F}$$

Glass $Y_S t_S >> Y_F t_F$

$$\varepsilon_S = \varepsilon_F \frac{Y_F t_F}{Y_S t_S} << \varepsilon_F$$

Plastic; $Y_S t_S \sim Y_F t_F$

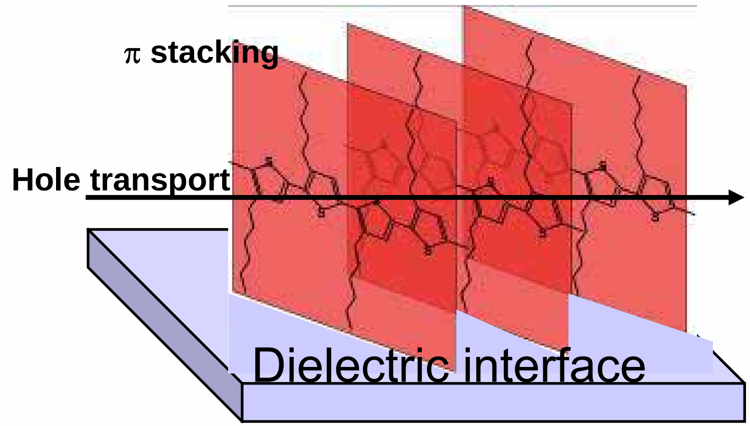
$$\varepsilon_S \approx \varepsilon_F$$

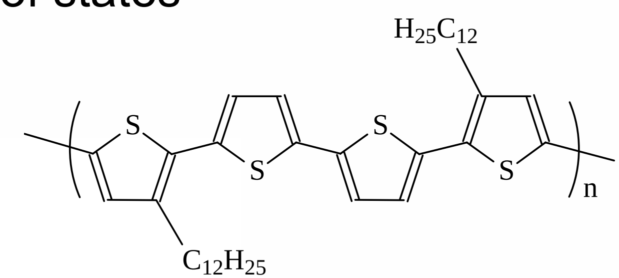
TFT mobility

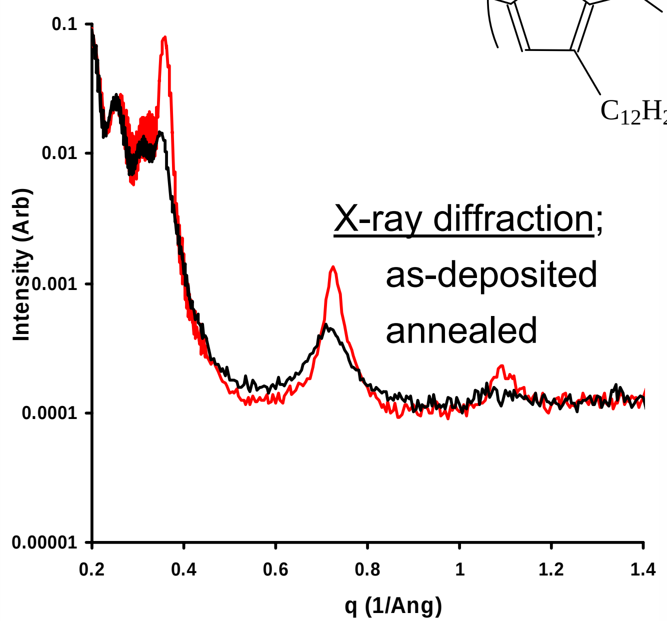
- Physical structure of films
  - Dielectric interfaces
- Electronic structure
  - Density of states
- Transport models

High mobility polymer semiconductors

- π stacked lamella structure
- Highly oriented crystalline film
  - 10-100 nm ordered regions
  - Separated by amorphous material
- Transport in ~1 molecular layer
  - 2-d density of states

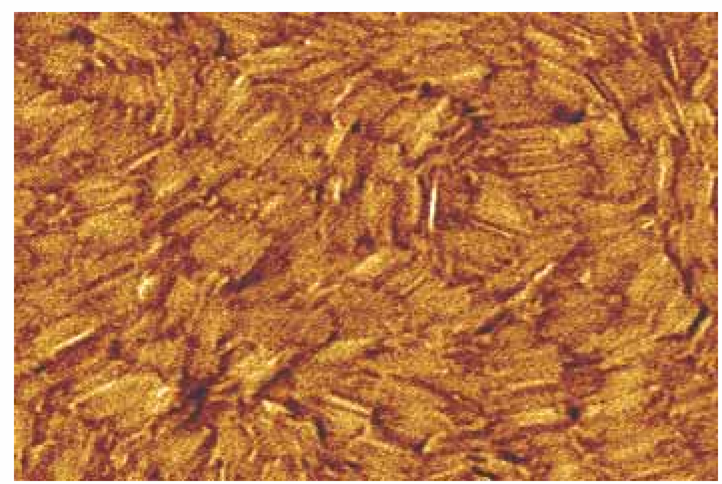






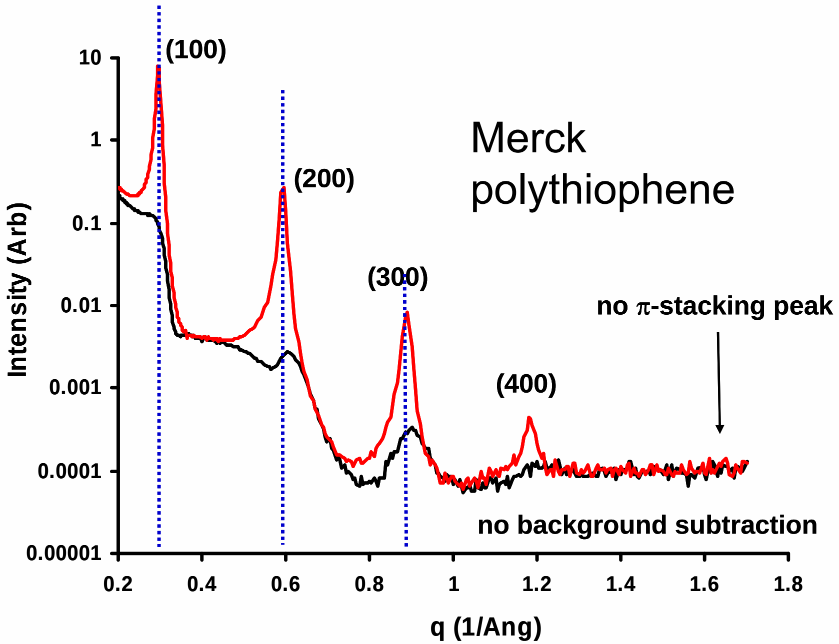
X-ray measurement of ordered structure

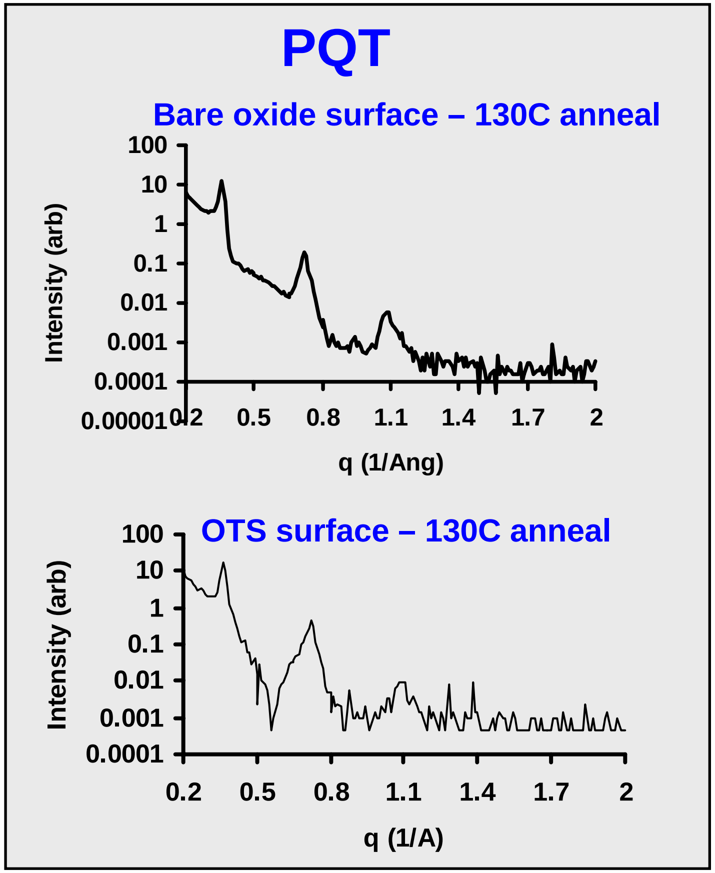
AFM image of PQT



X-ray diffraction data

- Lamellar ordering and (hopefully) crystal structure
  - Highly ordered material is best (?)
- PQT out of plane x-ray has similar scattering for OTS and bare Si, but mobility is 1000x different
  - What happens at the interface?





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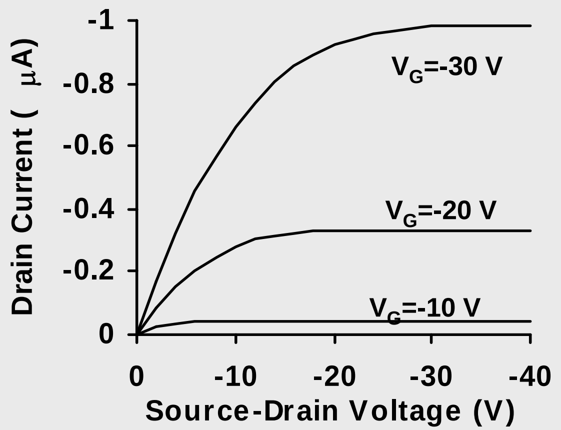
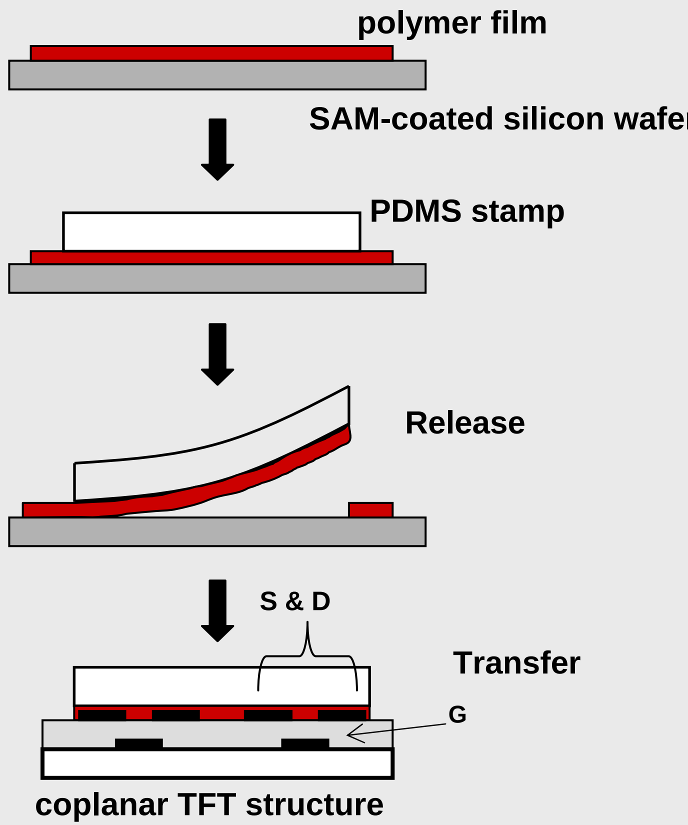
Studying interfaces by delamination

- Polymer layer can be transferred from one surface to another
- Transfer from SAM-coated surface to TFT structure
  - comparable TFT performance as spin-coated films
- Test role of surface to determine structure
  - Transfer then anneal

TFT characteristics of transferred TFT





Chabinyc et al. JACS, 126, 13928, 2004.

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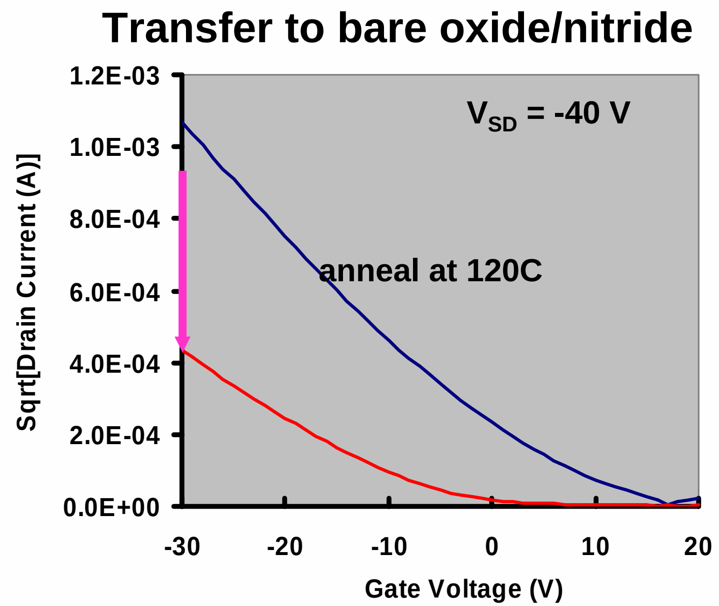
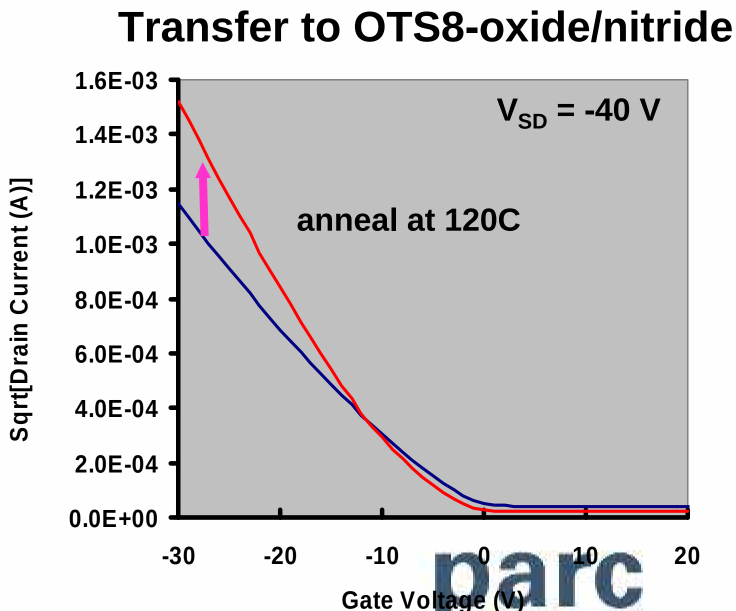
Transferred TFTs

- Transfer to bare oxide dielectric
  - Starting mobility ~0.015-0.03 cm^2/Vs
  - mobility decreases on annealing
- Transfer to oxide + OTS
  - mobility increases on annealing

- The polymer surface structure is ~stable at room temperature
  - 120C anneal allows structural change
- Structure controlled by energetics, not kinetics
  - The equilibrium structure depends on the surface hydrophobicity





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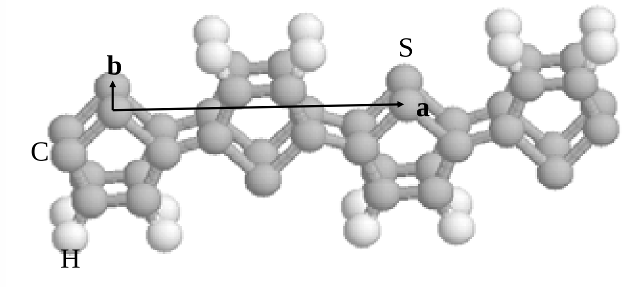
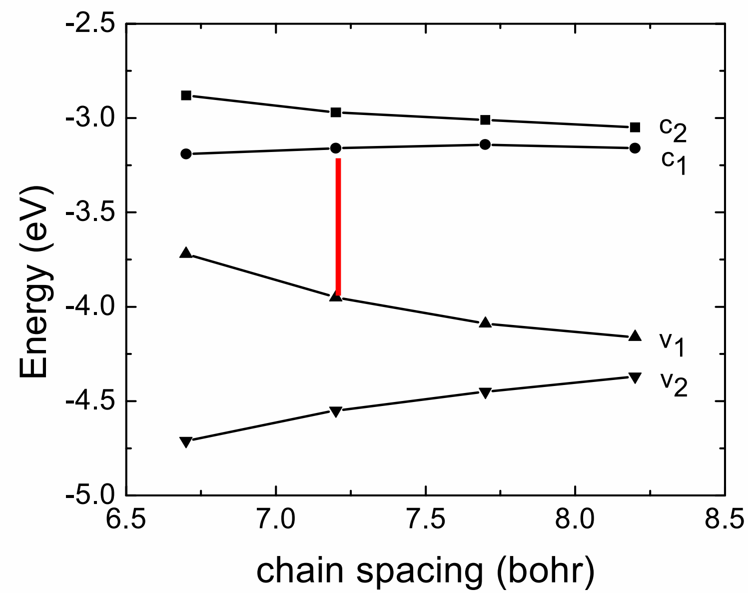
Electronic structure calculations

- LDA calculations of crystalline structure
  - no electron-phonon interaction
- π-π interaction widens bands
- Valence band shifts w.r.t. amorphous material by ~0.3 eV
- 2-dimensional DOS
  - 2×10^{14} cm^{-2} eV^{-1}
- Estimate of RT mobility
  - Acoustic phonon scattering
  - μ_0 ~ 10 cm^2/Vs in π direction

$$\mu = \frac{2\pi\hbar^4 Be}{\varepsilon_{ac}^2 (3kT)^{3/2} (m^*)^{5/2}}$$





Change of band edges with chain spacing

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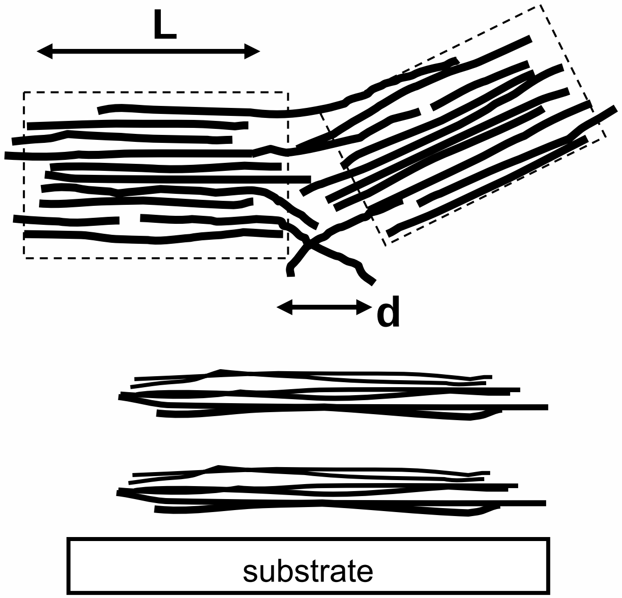
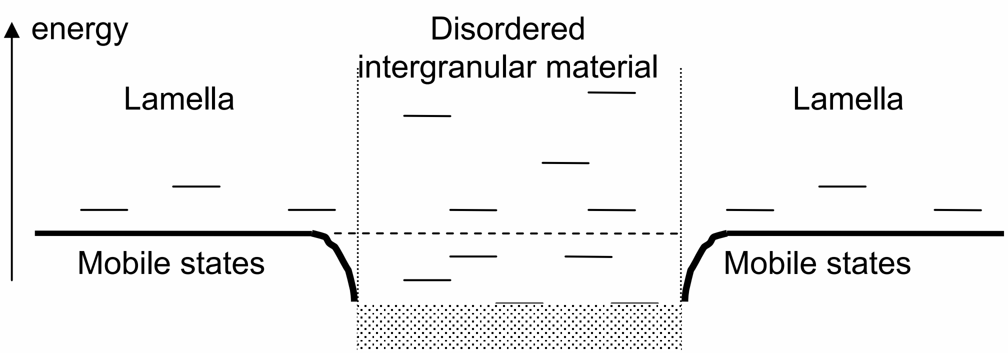
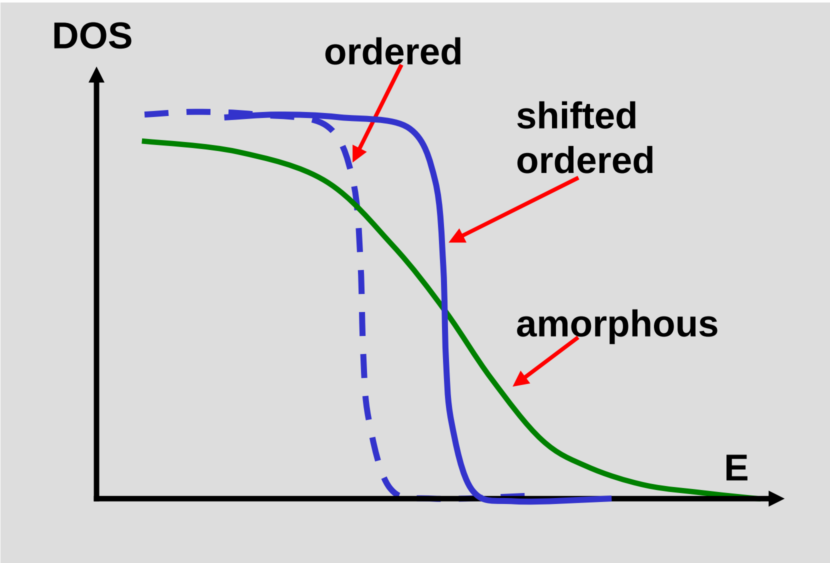
DOS for mixed phase material

- Amorphous fraction = *2d/L*
  - At least 10-20%
- Shift of band edge
  - ~0.3 eV
  - barrier to the amorphous region

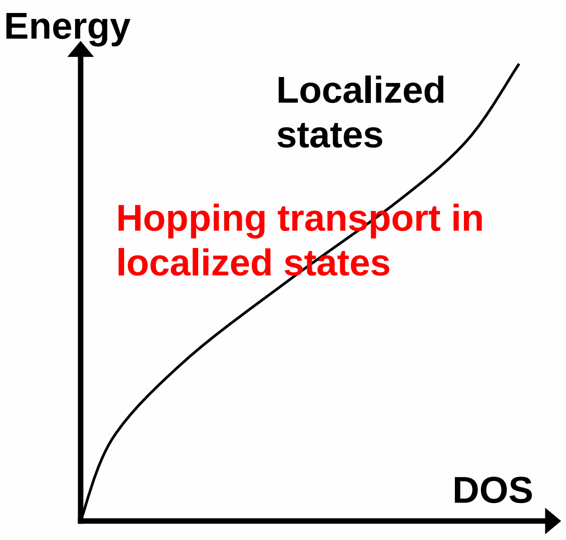


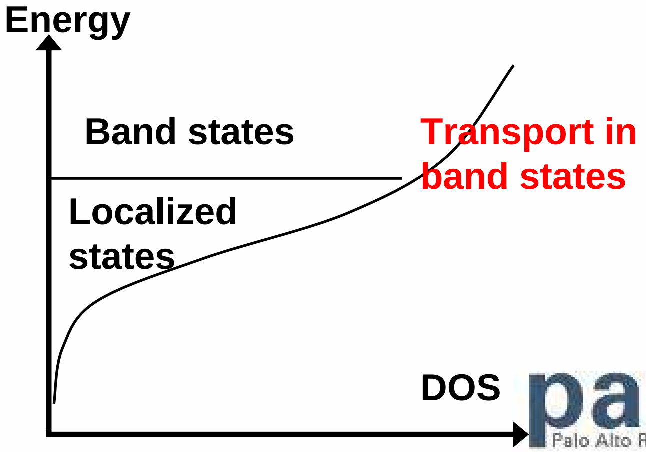




Transport processes

- Amorphous polymers
  - Hopping in broad band of localized states
  - Low mobility
- Single crystal organics
  - Band transport
- Polycrystalline polymers
  - Mixture of amorphous and crystalline
  - What role does each have in the transport?
  - How do you know?





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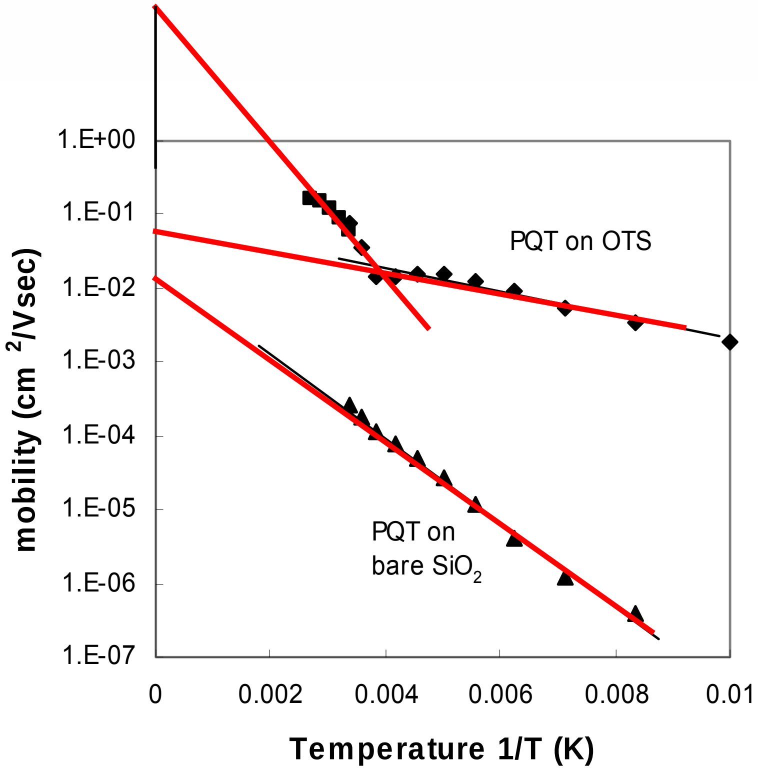
Transport in PQT

- Thermally activated transport
- High mobility material has much higher prefactor (~ 500 cm^2/Vs)

  $\mu = \mu_{PRE} \exp[E_T/kT]$.

  – Implies high band mobility and high DOS
- Low mobility material has low prefactor

  – Implies a different transport process



Statistical shift

$$\mu_{PRE} = \frac{\mu_0 N_V kT}{n_T} \exp\left(-\gamma_T / k\right)$$

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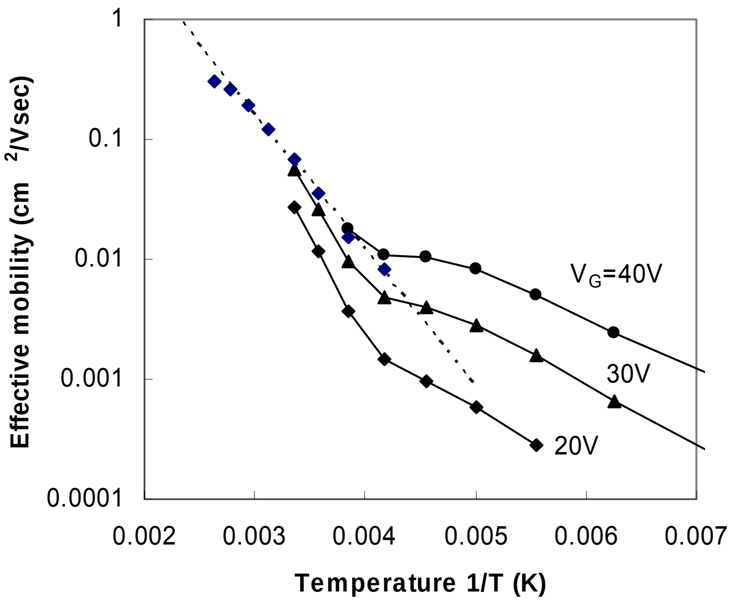
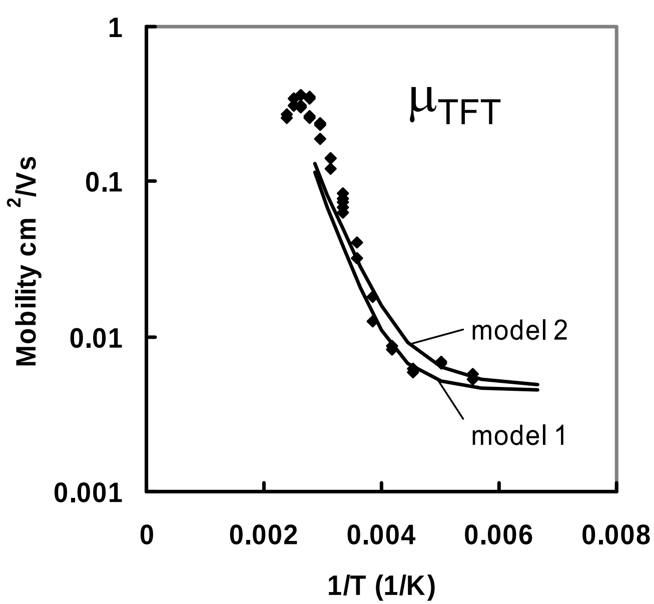
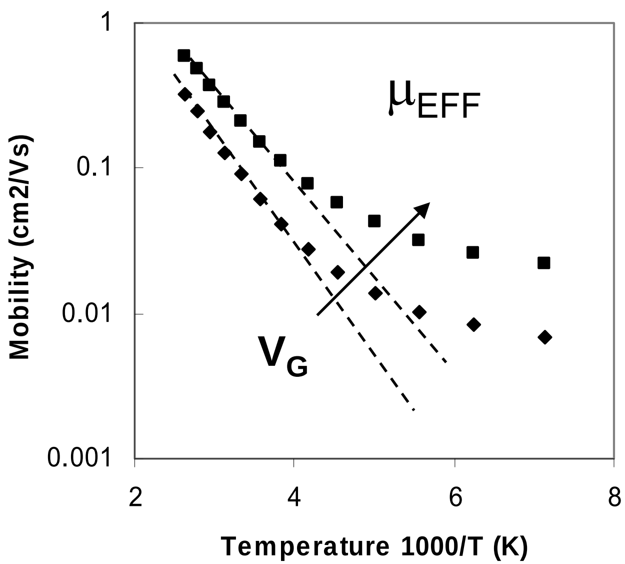
Transport model calculations

- Model can fit the mobility and T-dependence
  - reasonable value of prefactor
- Change of slope explained by transport in amorphous regions



Calculated versus measured conduction data



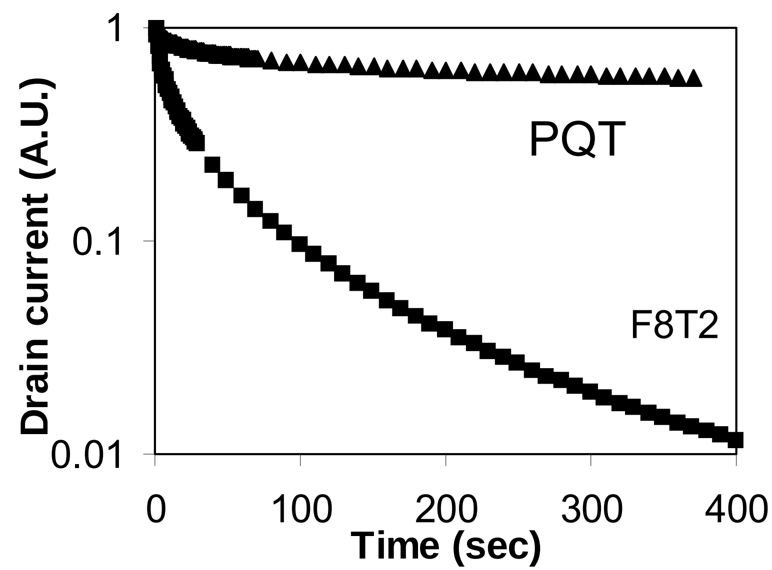


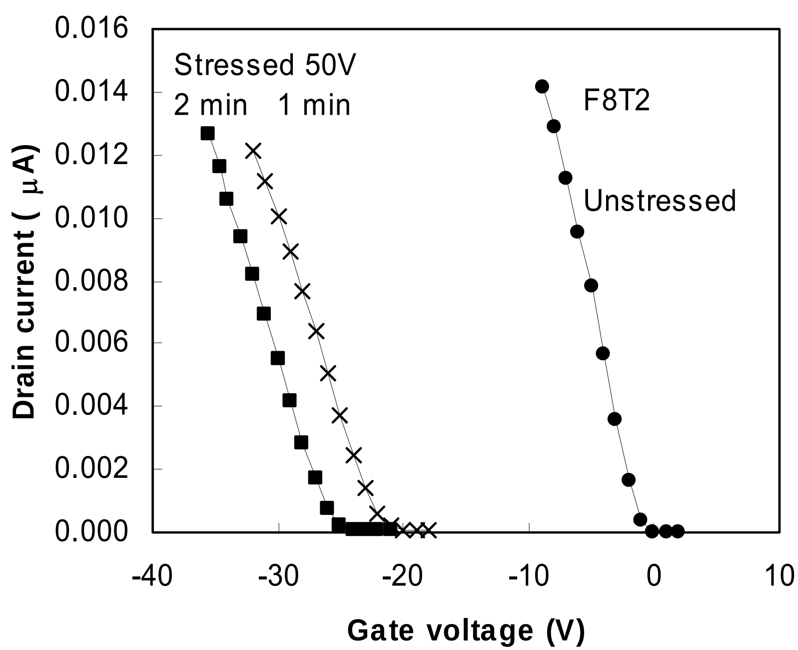
Lifetime

- Bias stress
- Chemical

Bias-stress effects

- Threshold voltage shift; no change in mobility
  - Slow charge trapping
- Effect in the polymer, rather than the SAM or the dielectric
  - Depends on the polymer
  - Independent of dielectric





PQT: initial stress reverses quickly

F8T2; stable stress, reversed by

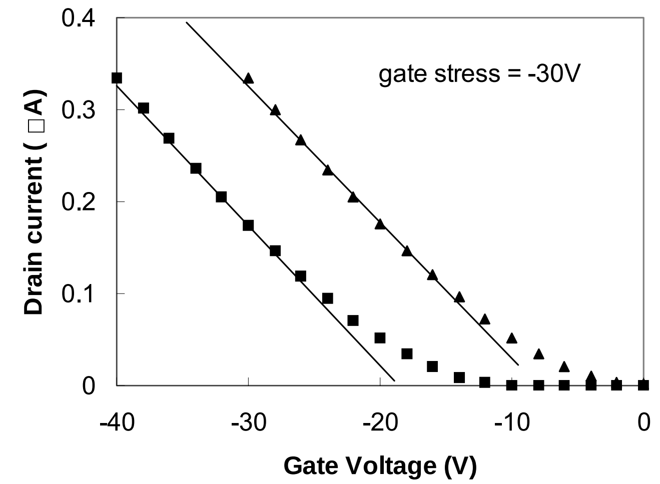
-Illumination

-annealing

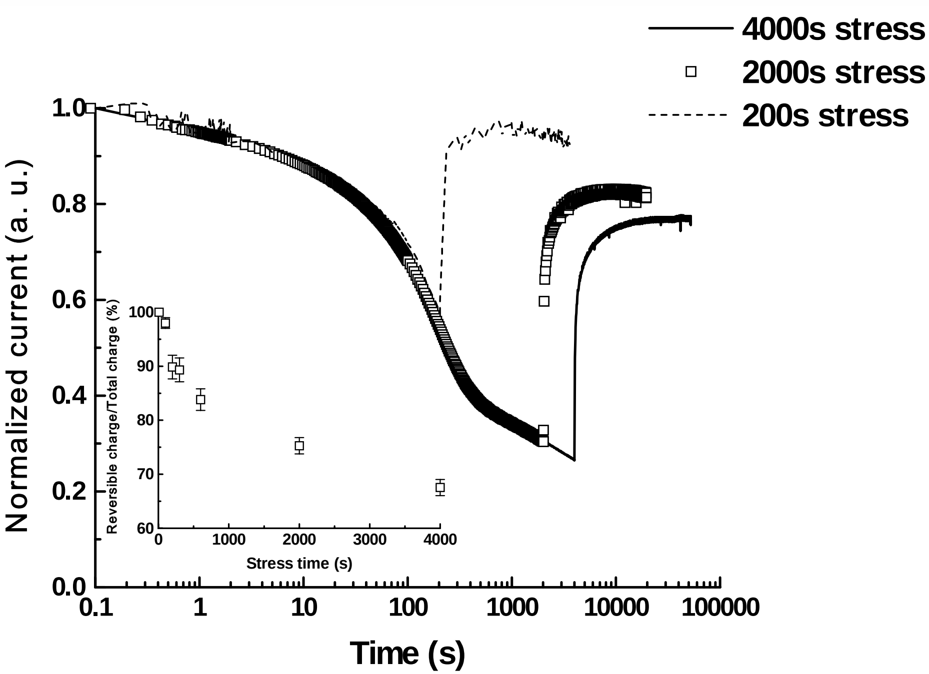
Bias stress in polymer TFTs

Fast and slow stress effects in PQT

- Threshold voltage shift



- Fast process;
  - Stress occurs in a few seconds
  - Reverses equally quickly
  - Not important for TFT arrays
- Slow process
  - Dominates after 100s-1000s sec
  - Reverses slowly

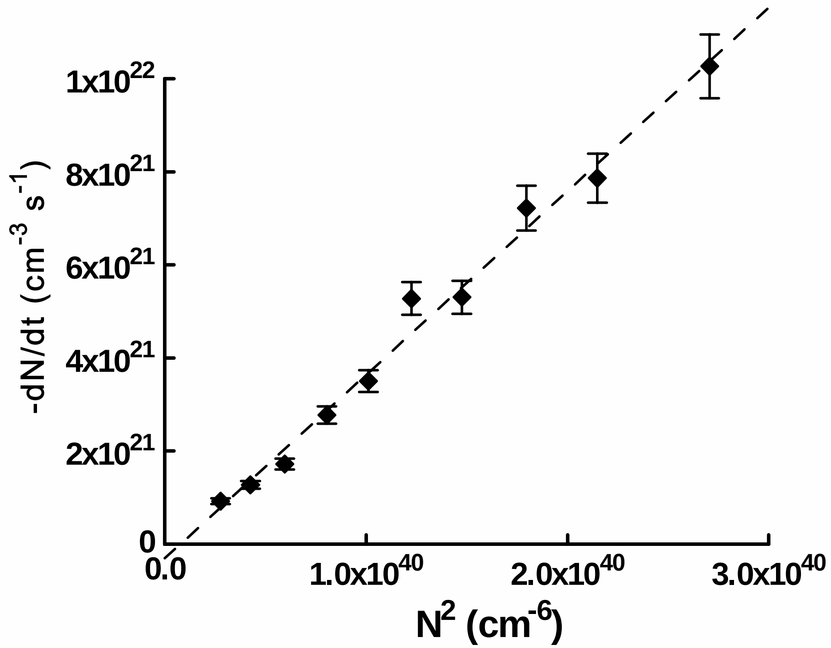


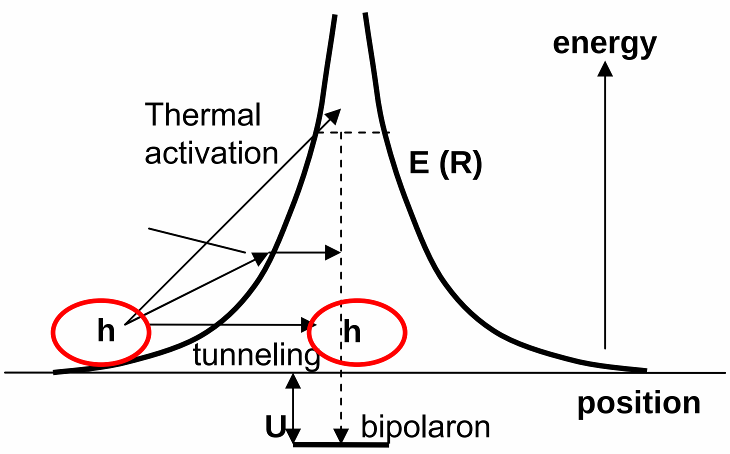
Bias-stress effects

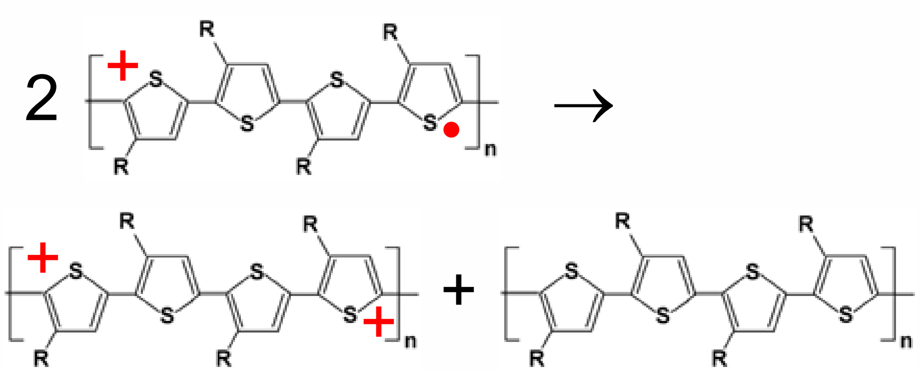
- Second order trapping kinetics

  $$dN_H/dt = k\, N_H^2$$

- Pairs of holes interact and trap
  - Bipolaron (h + h ↔ BP)
  - Stabilized by structural relaxation
- Trapping rate is slow because of Coulomb repulsion
  - Tunnelling mechanism?

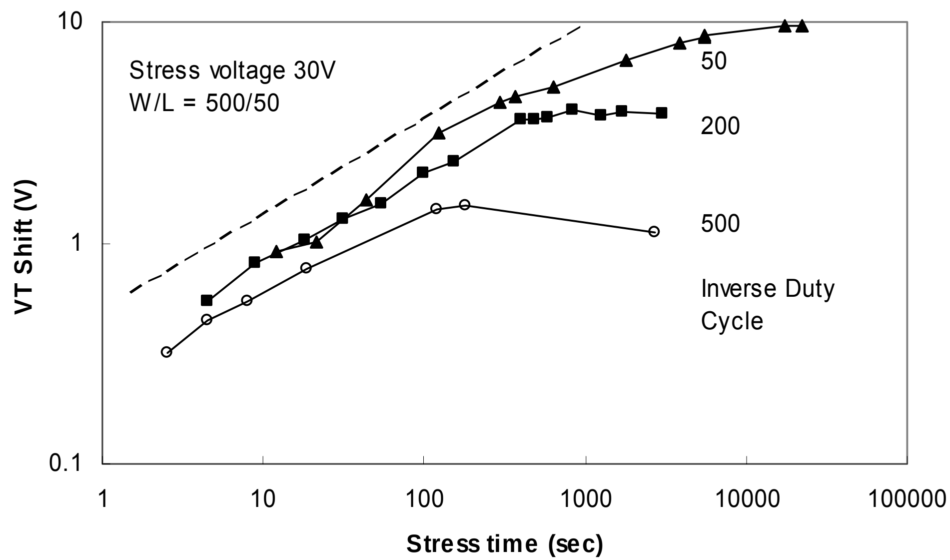


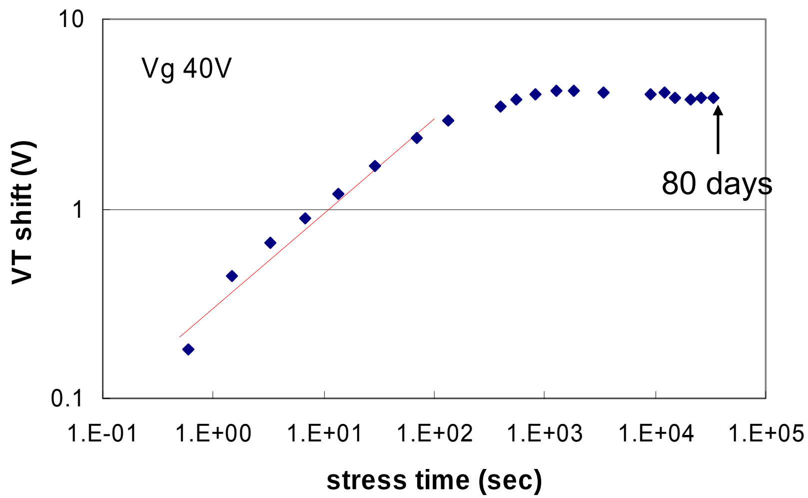


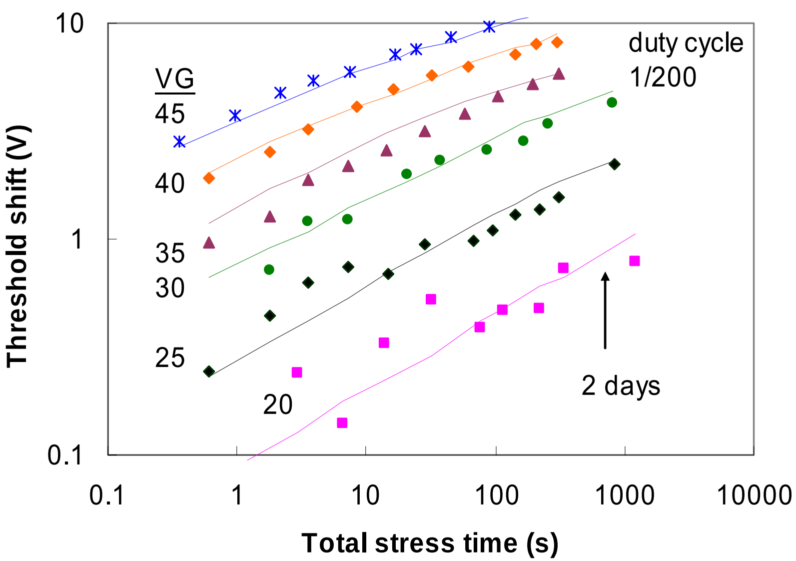


Slow bias stress in PQT

- At low duty cycle
  - Slow process only
  - V_T shift increases as power law t^{α}, α =0.3-0.5
  - V_T shift saturates due to slow recovery
- Recovery time constant ~100 hours at 300K







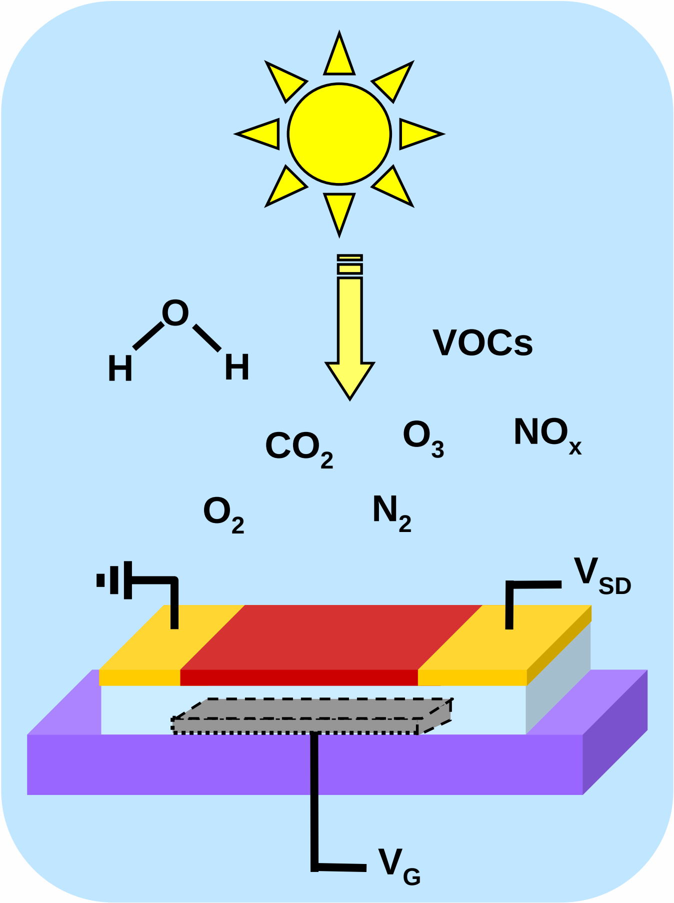
Environmental Stability

- Photo-induced effects
  - photocurrent under operation
  - photooxidation from 1O2

light shielding solves most problems

- Impurities
  - contamination during fabrication
  - adsorption from the environment

difficult to control;
unknown effects for long-term stability



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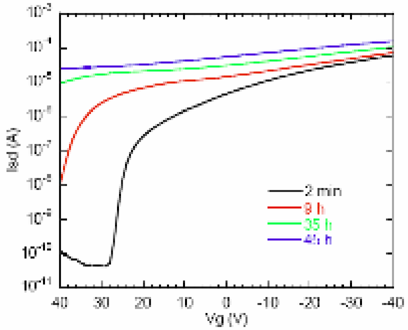
Doping in the Ambient

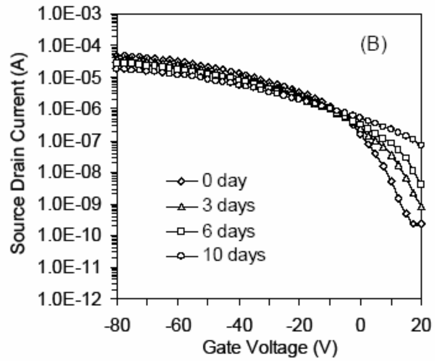
"well-known that P3HT is doped by oxygen exposure"

Merck - ambient



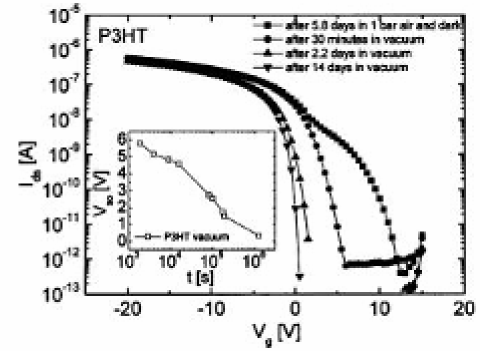
M. Heeney, et. al. *J. Am. Chem. Soc.*; **2005**

XRCC – ambient



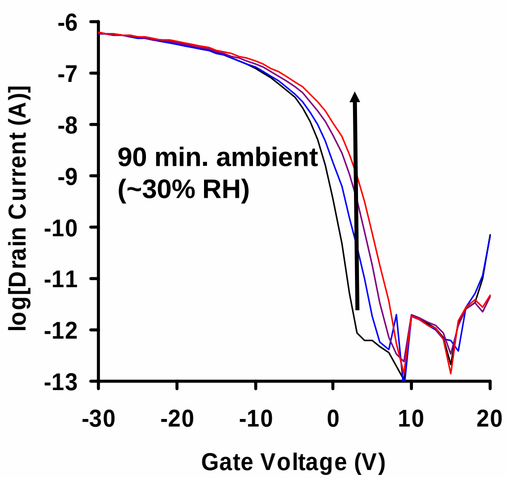
B.S. Ong, et. al. *J. Am. Chem. Soc.*; **2004**

Philips – "dry air"

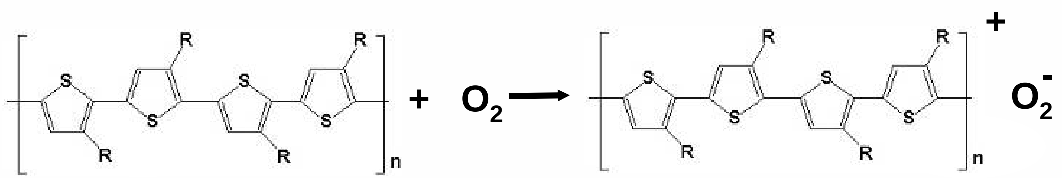


E. Meijer, et. al. *J. Appl. Phys*. 2003

PARC – PQT-12 in ambient



charge transfer complex known for P3HT



$\Delta G \sim -0.02$ eV

solubility of O_2 in P3HT at
atmospheric conc. ~0.2 % volume
Abdou, Holdcroft *JACS* 1997

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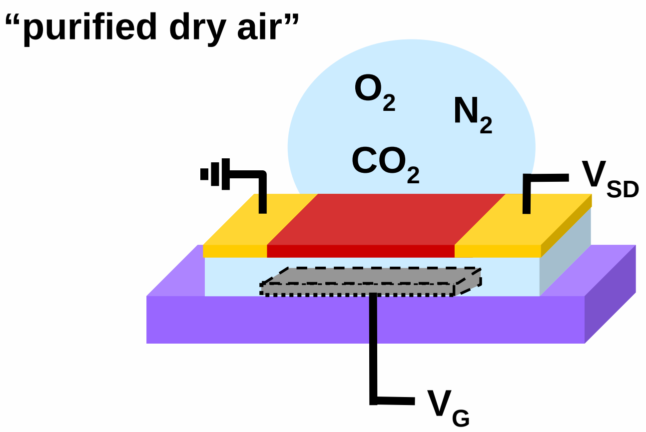
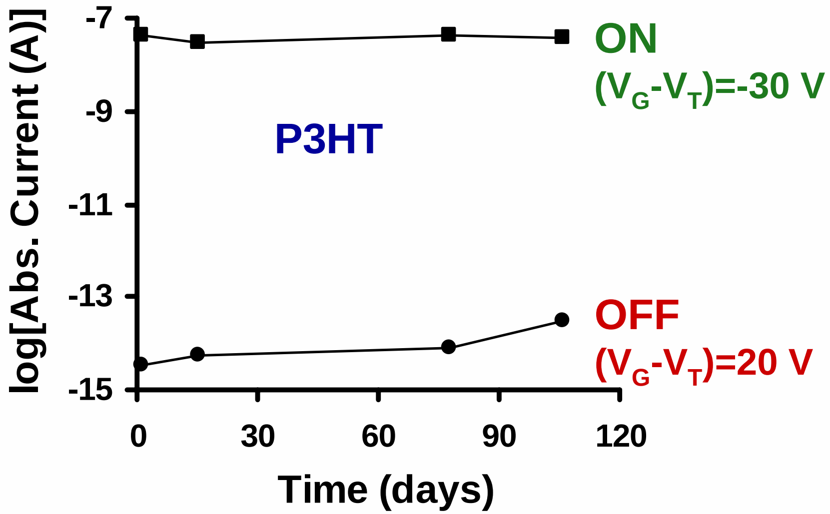
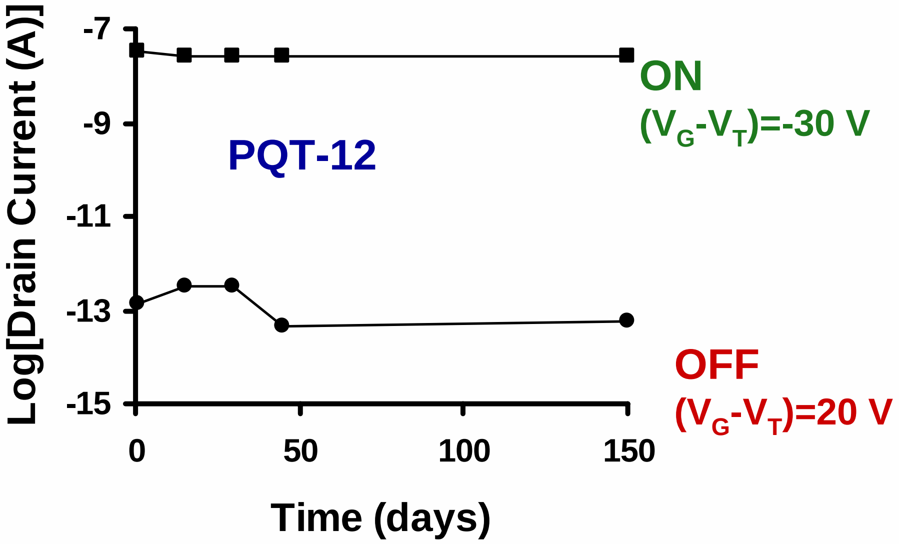
TFT operation in clean dry air

- Oxygen is evidently not a strong dopant for polythiophenes
- Air effect must be impurities







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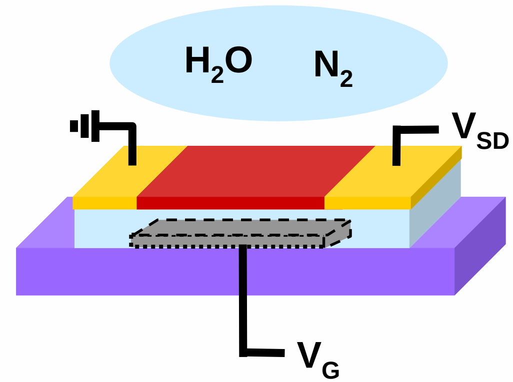
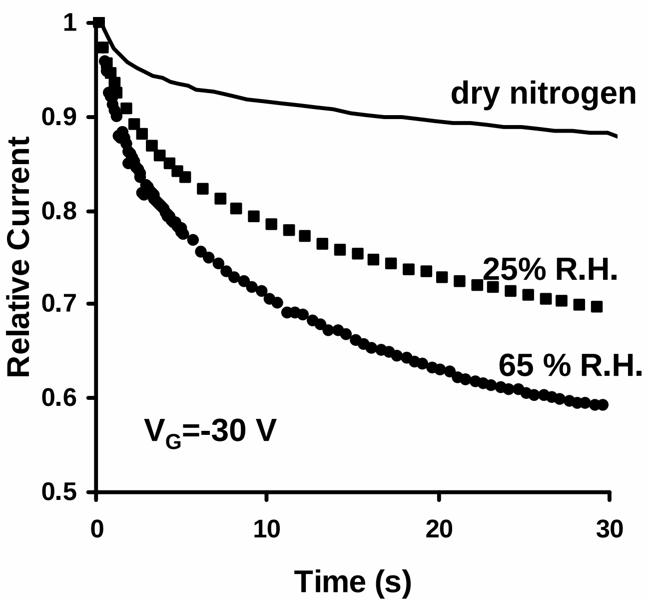
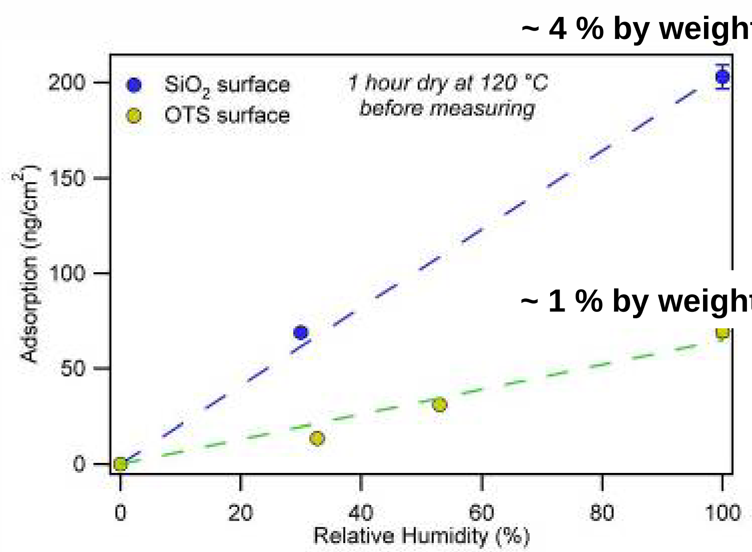
TFT operation in the water vapor

- Mobility is relatively unaffected
- Bias stress effect is enhanced







at 30% R.H.
~20 ng/cm^2 water for
~ 50 nm thick PQT-12 film (5000 ng/cm^2)

so ~1 x 10^{13} H_2O/cm^2 in 1 nm
at V_G =-30 V , C~ 30 nF/cm^2 , ~ 5x 10^{12} holes/cm^2

$$\frac{\textbf{H}_2\textbf{O molecules}}{\textbf{holes}} \sim 2\text{-}5$$

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Some questions

- What is the structure at different length scales?
- Why does a SAM improve the a TFT?
- What is the role of surface roughness?
- Can we model the transport accurately
- How would you design a polymer to have a higher mobility?
- What is the mechanism of bias-stress; does it depend on film contamination?
- What ambient impurities are affecting the TFT and how can they be prevented?